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High-pressure phase behaviour of two poly-aromatic molecules in the presence of toluene and carbon dioxide

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ABSTRACT

Asphaltene precipitation and deposition is a serious problem in oil recovery, oil transportation and refinery operations. Understanding of the phase behaviour of systems containing asphaltenes is very important to develop effective asphaltene deposition mitigation strategies. In order to get a better understanding of asphaltenes and in particular to get more insight in relations between molecular structural features and observed macroscopic behaviour, the phase behaviour of two poly-aromatic molecules (violanthrone-79 and hexa-tert-butylhexa-peri-hexabenzocoronene) was studied. Although both compounds do not represent all specific features of real asphaltenes, it is expected that to some extend they do. For instance, real asphaltenes are ill-defined mixtures and hard to characterize, while the selected poly-aromatic compounds form a well-defined system with toluene and CO_2. The poly-aromatic compounds were selected based on their molecular features and their tendency to self-assemble. The phase behaviour of solutions of these compounds in toluene was studied in the presence of different concentrations of carbon dioxide with a so-called Cailletet apparatus. The results in this work showed that the concentration of carbon dioxide affects the precipitation of the poly-aromatic compounds. At low concentration there is no precipitation, i.e., carbon dioxide acts as a co-solvent, while at higher concentration, carbon dioxide acts as an anti-solvent and the poly-aromatic molecule in the ternary system precipitates. As far as the phase behaviour is concerned, hexa-tert-butylhexa-peri-hexabenzocoronene resembles that of a real asphaltene.

1. Introduction

Asphaltenes are often defined as a solubility class, i.e., it is the petroleum fraction that is insoluble in light alkanes, such as *n*-heptane, but soluble in toluene [1,2]. They are the heaviest and most polar components in crude oil with the highest hetero-atoms content [3,4]. There is a common understanding that asphaltene components consist of fused aromatic rings with substituents like alkyl chains and naphthene rings originating from the edges of the fused structure of aromatic rings. Research has confirmed that even in good solvents asphaltenes are present as nano-aggregates at very low concentrations, most likely due to interactions between the fused ring systems of individual molecules and that these nano-aggregates can further assemble to small clusters under increasingly poor solvent conditions [5,6]. The formation of these asphaltene clusters is a major problem for the oil industry as they can deposit and block critical parts in the oil production systems, resulting in production interruption and major economic losses.

Since asphaltenes are defined as a solubility class, this fraction covers a range of different components. This range is highly dependent on the precipitation method that is used for extraction and also the nature of the crude oil as well [7,8]. Hence, asphaltenes are a complex and ill-defined component class and it explains, to some extent, why we still have an incomplete understanding about this petroleum fraction. This, in turn, makes it difficult to develop effective asphaltene deposition mitigation strategies. The aim of this work is to get a better understanding of real asphaltenes by studying well-defined systems consisting of poly-aromatic compounds that have certain features in common with real asphaltenes.

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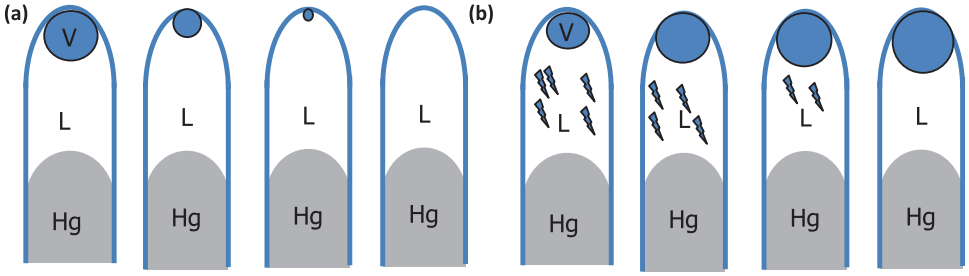

Fig. 1. (a) Liquid–vapour to liquid phase change in the Cailletet tube. From left to right, pressure is increased at constant temperature. (b) Solid–liquid–vapour to liquid–vapour phase change. From left to right pressure is decreased. L, liquid phase; V, vapour phase; (graphic symbol) solid phase; Hg, mercury.

In particular, we are interested in obtaining insight in the relation between molecular structure and observed phase behaviour at various pressures, temperatures and compositions. In literature similar investigations have been reported with more complex mixtures that are still not well-defined. For example, Andersen and Speight [9] looked at asphaltene systems where the asphaltene was precipitated with *n*-pentane and dissolved in higher *n*-alkanes. Orangi et al. [10] studied systems in which the asphaltene was represented by a polymer with crude oil as the solvent. The model systems that will be explored in this study are properly defined, i.e., we know precisely which components are present and in which concentration.

The model compounds that are used for the experiments are chosen based on their structural features. Like real asphaltenes, they should consist of a core of fused aromatic rings with peripheral side chains. In addition, the model compounds should have the tendency to show self-assembly. Certain dyes are substances used in the paint industry and also have been applied in fluorescence studies as model molecules for asphaltenes [11]. They are usually very aromatic and also contain a number of hetero-atoms, which can lead to a complex mechanism of self-association, forming aggregates of variable size. In this work, violanthrone-79, a dye molecule, was selected to be used as a poly-aromatic molecule to mimic certain features asphaltene molecules. This molecule represents an asphaltene of continental type with a large aromatic region plus side chains [11,12].

Hexabenzocoronenes have been studied intensively, because of their promising p-type semi-conductivity, which is a result of their large aromatic core and strong self-association. These types of molecules consist of a large number of fused six-membered aromatic rings which can be substituted with different side chains. Because of its molecular structure and tendency to self-assemble, the hexabenzocoronene derivative hexa-tert-butylhexa-peri-hexabenzocoronene was another selected poly-aromatic molecule to mimic a limited number of features of asphaltene molecules. Hexabenzocoronene, containing 13 fused aromatic rings, can self-assemble into columnar structures [13,14].

In this work, the influence of certain CO_2-concentrations on the phase behaviour of the two selected poly-aromatic compounds dissolved in toluene is studied as CO_2 is commonly applied as an injection fluid for enhanced oil recovery. This method is one of the most efficient oil development methods because carbon dioxide can decrease the viscosity of crude oil, and reducing interfacial tension between the displacing and displaced phase [15].

2. Experimental

2.1. Apparatus and procedures

The experimental work has been carried out in a Cailletet apparatus. For a detailed description of the Cailletet apparatus and the operating methods one is referred to de Loos et al. [17]. In this apparatus the pressure (or temperature) can be varied at fixed temperature (or pressure) for a sample with a constant overall composition until a phase transition is visually observed. The pressure and temperature range for this setup are 3.5 bar up to 140 bar and 250 K up to 450 K, respectively. The main part of the apparatus is a thick-walled Pyrex glass tube of which one end is closed and the other end is open. The sample is confined with mercury in the top of the closed end of the tube. The Cailletet tube was filled with a sample with known overall composition. The sample in the tube was degassed by freezing and melting the sample under vacuum. After degassing, a known volume of carbon dioxide was added to the mixture, sealed with mercury and finally connected to the high-pressure system of the autoclave. The amount of moles of carbon dioxide in the calibrated vessel was calculated by applying the ideal gas law. The sample was stirred during the measurements by using a stainless steel ball which is moved by two button magnets. In order to have a constant temperature, a water bath was used with an accuracy of 0.02 K. Pressure is generated with the help of a screw type hand pump. A dead weight pressure gauge is used to measure the pressure inside the tube. The accuracy of the pressure measurements is within 0.03% of the reading.

Solutions of violanthrone-79 and hexa-tert-butylhexa-peri-hexabenzocoronene in toluene were prepared. For both solutions the concentration of the poly-aromatic compound amounted 0.3424 mass%. This concentration was used for all experiments. Although the solubility of both violanthrone-79 and hexa-tert-butylhexa-peri-hexabenzocoronene in toluene is significantly higher, more elevated concentrations of these components would have resulted in solutions that are too dark for visual observation of the phase transitions in the Cailletet apparatus. The schematic representation of the observed phase transitions is shown in Fig. 1.

2.2. Materials

Violanthrone-79 (purity >95%), toluene (purity >99.5%) and carbon dioxide (purity >99.99%) were obtained from Sigma–Aldrich, ACROS and Hoek-Loos, respectively. All chemicals were used without further purification. Hexa-tert-butylhexa-peri-hexabenzocoronene was synthesized in the laboratory. The synthesize procedure is described by Rathore and Burns [18]. The molecular features of violanthrone-79 and hexa-peri-hexabenzocoronene are shown in Figs. 2 and 3.

3. Results and discussion

Tables 1–4 show the primary experimental data of various phase transitions, i.e., vapour–liquid, solid–liquid–vapour, and solid–liquid for the system of violanthrone-79 and toluene. In addition, the graphical representations of the experimentally determined phase behaviour are shown in Figs. 4–7. Fig. 4 shows the transition of liquid–vapour to liquid (bubble points) for different concentrations of CO_2. From this graph it can be observed that